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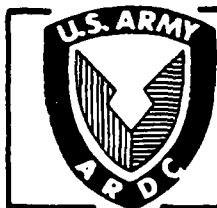
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EMBRITTLEMENT OF GUN STEEL BY COPPER

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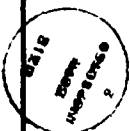
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20. ABSTRACT (CONT'D)

using capacitance discharge heating verified that copper-induced embrittlement and cracking can occur during a thermal pulse of only a few milliseconds duration. Hot tensile testing with a Gleeble machine confirmed that copper penetrates austenite grain boundaries causing hot tearing in just a few seconds at 1000°C, i.e., well below the melting point of copper.



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INTRODUCTION

During firing, the bore surfaces of cannon tubes are subjected to very brief (10-20 millisecond duration) but very damaging exposure to high flame temperatures (2-3000°K) and intense thermo-mechanical stresses (50,000 psi) in extremely reactive propellant gases. These conditions cause severe cannon barrel erosion and cracking that has been the subject of extensive and long-standing research at Benet Weapons Laboratory and other laboratories (refs 1-4). Our previous studies (ref 4) were largely concerned with the chemical alterations of the surface stemming from the highly carburizing nature of the spent propellant gases but they also suggested that thermal cracking is aggravated by the effects of Cu-induced embrittlement.

The principal results of the previous investigation are illustrated by the representative optical micrograph of a nickel-plated, polished, and etched cross-section of a fired cannon barrel shown in Figure 1. Four features may be noted: (1) an etch-resistant "white layer" along the surface, (2) regularly spaced shallow cracks in the white layer, (3) occasional very deep cracks penetrating into the steel matrix, (4) a heat-affected zone where very

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- ¹I. Ahmad, "The Problem of Gun Barrel Erosion - An Overview," Proceedings of the Tri-Service Gun Tube Wear and Erosion Symposium, Jean-Paul Picard and Iqbal Ahmad, Eds., ARRADCOM, Dover, NJ, 29-31 March 1977, pp. 1-50.
 - ²R. B. Griffin, J. P. Pepe, and C. Morris, "Metallurgical Examination of Bore Surface Damage in a Five-Inch Gun," Metallography, Vol. 8, 1975, pp. 453-471.
 - ³M. H. Kamdar, A. Campbell, and T. Brassard, "A Metallographic Study of White Layer in Gun Steel," ARRADCOM Technical Report No. ARLCB-TR-78012, Benet Weapons Laboratory, Watervliet, NY, August 1978.
 - ⁴R. M. Fisher, A. Szirmai, and M. H. Kamdar, "Metallographic Studies of Erosion and Cracking of Cannon Tubes," Proceedings of the Tri-Service Gun Tube Wear and Erosion Symposium, ARRADCOM, Dover, NJ, 26 October 1982.



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Figure 1. Photomicrograph of nickel-plated, polished, and etched cross-section of a fired cannon tube showing white layer and cracks.

fine carbides have formed. Various analytical and metallographical techniques were used to determine the identity, composition, and structure of phases at and near the surface. It was found that the steel surface is highly carburized to the point of formation of a thin (1-2 μm) layer of cementite overlaying a subsurface region (10-20 μm) of high carbon austenite (1% C) to comprise the etch-resistant "white layers". Large differential contraction between the surface austenite and the ferrite results in high tensile stresses and cracking of the surface during cooling after the firing cycle. Point to point energy dispersive x-ray analyses (EDXS) during scanning electron microscope (SEM) examination of fired cannon revealed the presence of significant quantities of copper on the bore surface and in the cracks. This discovery prompted a more detailed study of the apparent role of Cu in the

cracking of cannon barrels. In addition to metallographic analysis of fired cannon tubes, a unique apparatus (ref 3) designed and constructed to simulate firing conditions in the laboratory and a Gleeble hot tensile machine were utilized to prepare specimens for the study.

METALLOGRAPHIC OBSERVATIONS

Fired Cannon Tubes

Visual inspection of the bore surface of fired cannon tubes revealed the occurrence of extended abrasion marks parallel to the rifling as illustrated in Figure 2(a). These abrasion marks which are not readily discernible because of wear of the cannon tube, are spaced about 1 cm apart which corresponds to the separation of the rectangular corrugations on the Cu rotating band on the projectile which engages the rifling on the bore to impose a twisting movement to the projectile. It may also be noted on the figure that the longitudinal cracks are also parallel to abrasion marks and not the bore axis. A SEM image of the bore surface of this sample is shown in Figure 2(b) illustrating the corn-cob-like structure of the heat check pattern and an example of a deeply penetrating longitudinal crack. The EDXS spectrum from this area included in the figure shows the presence of Al, S, K, Ti, and Cu in addition to Fe from the steel base. Point to point EDXS analysis showed that the surface is coated with Ti and the other elements present in the propellant except at some region in the center of the figure where they were

³M. H. Kamdar, A. Campbell, and T. Brassard, "A Metallographic Study of White Layer in Gun Steel," ARRADCOM Technical Report No. ARLCB-TR-78012, Benet Weapons Laboratory, Watervliet, NY, August 1978.

removed by contact by the rapidly moving rotating band. In this region the steel base was exposed by abrasion and Cu deposited as illustrated by the x-ray maps for Ti, K, Fe, and Cu of the lower left-hand region of Figure 2.

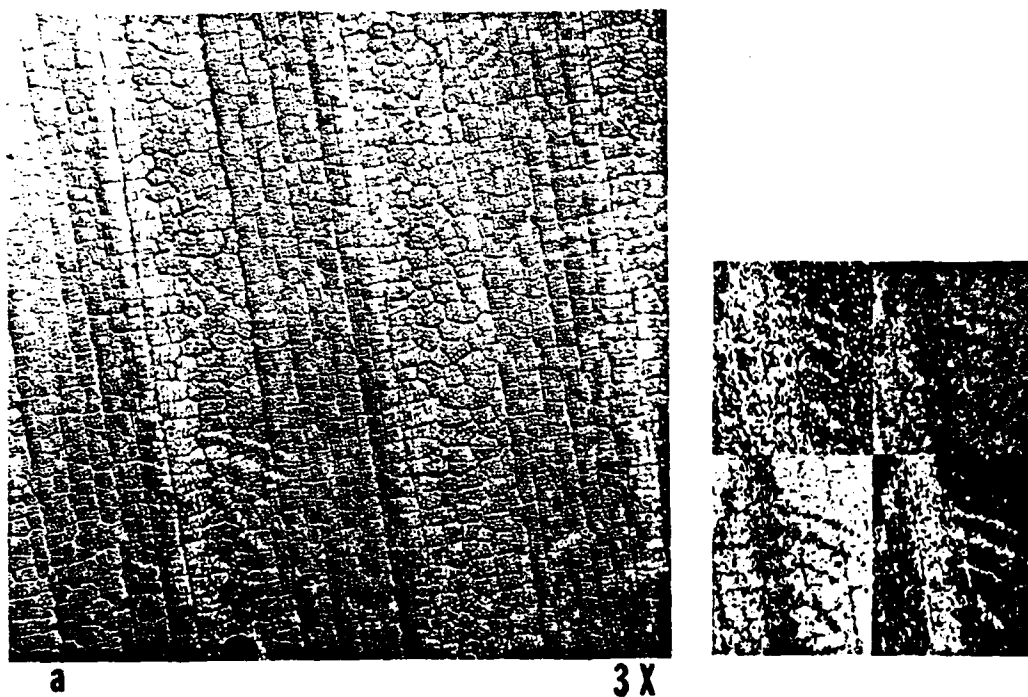


Figure 2(a). Photomicrograph and x-ray maps of bore surface of fired cannon showing Cu deposition along abrasion marks.

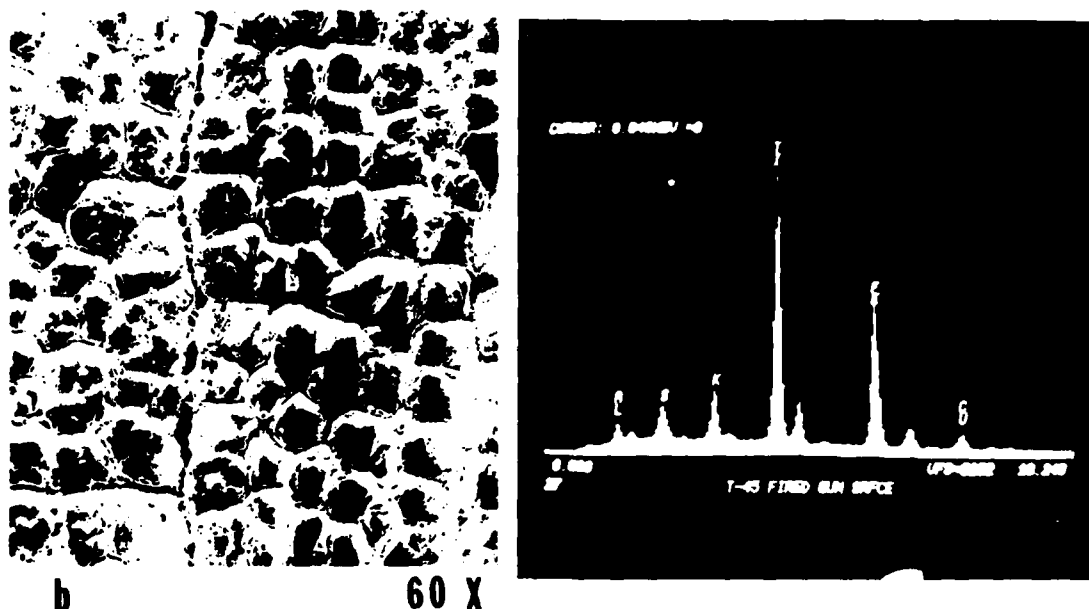


Figure 2(b). Scanning electron micrograph and x-ray spectra of the abrasion area. The surface is coated with TiO_2 which is added to the propellant.

A striking demonstration of the penetration of Cu into the deep cracks is illustrated in Figure 3. The micrograph in Figure 3(a) shows the bore surface of a fired cannon tube. The sample was mounted in a small clamp with the crack parallel to the jaws, chilled in liquid N_2 , and then fractured to expose the pre-existing crack surfaces. (The broken halves were reassembled for the micrograph in Figure 3(a).) One of the fracture surfaces and the corresponding x-ray map for Cu are shown in Figure 3(b). Penetration of Cu to the tip of the 0.4 mm deep crack is quite evident.

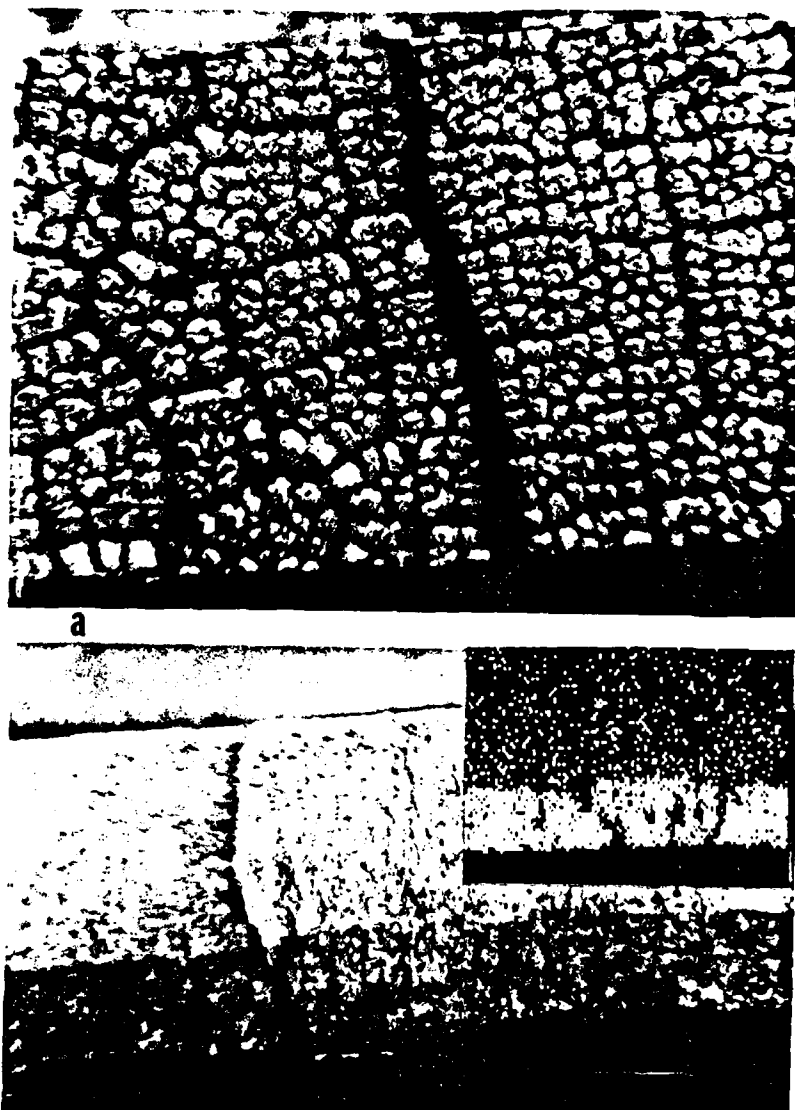


Figure 3. Photomicrograph (a) and x-ray map for Cu of fired cannon tube sample fractured under liquid nitrogen to expose surface of longitudinal crack.

Pulse Heated Specimens

A special pulse heating apparatus has been assembled at Benet Weapons Laboratory (ref 3) and used to successfully simulate the rapid heating and cooling gun steel (ASTM-A273 Grade 3), and the formation of white layer that occurs in several milliseconds during firing of a large cannon. The apparatus consists of a variable time-delay system for firing a parallel array of capacitors to make it possible to simulate a wide range of heating cycles in a high pressure atmosphere of methane or other gases if desired. This same apparatus was used to determine if the embrittling effects of Cu can occur during the short exposure intervals that occur during very rapid heating.

A low magnification photomicrograph of a notched and Cu-plated specimen after pulse heating near the melting point of copper is shown in Figure 4. Although the specimen was not heated to the melting point of copper, the "heat-affected" zone is clearly evident due to recrystallization of the copper plating. After polishing, a crack can be seen emanating from the root of the notch as shown in Figure 4(b) and after etching (Figure 4(c)). Faint traces of Cu were detected along the crack by EDXS. The effects were much more pronounced when specimens were heated above the melting point of copper but no cracking occurred with samples that were not Cu-plated.

³M. H. Kamdar, A. Campbell, and T. Brassard, "A Metallographic Study of White Layer in Gun Steel," ARRADCOM Technical Report No. ARLCB-TR-78012, Benet Weapons Laboratory, Watervliet, NY, August 1978.

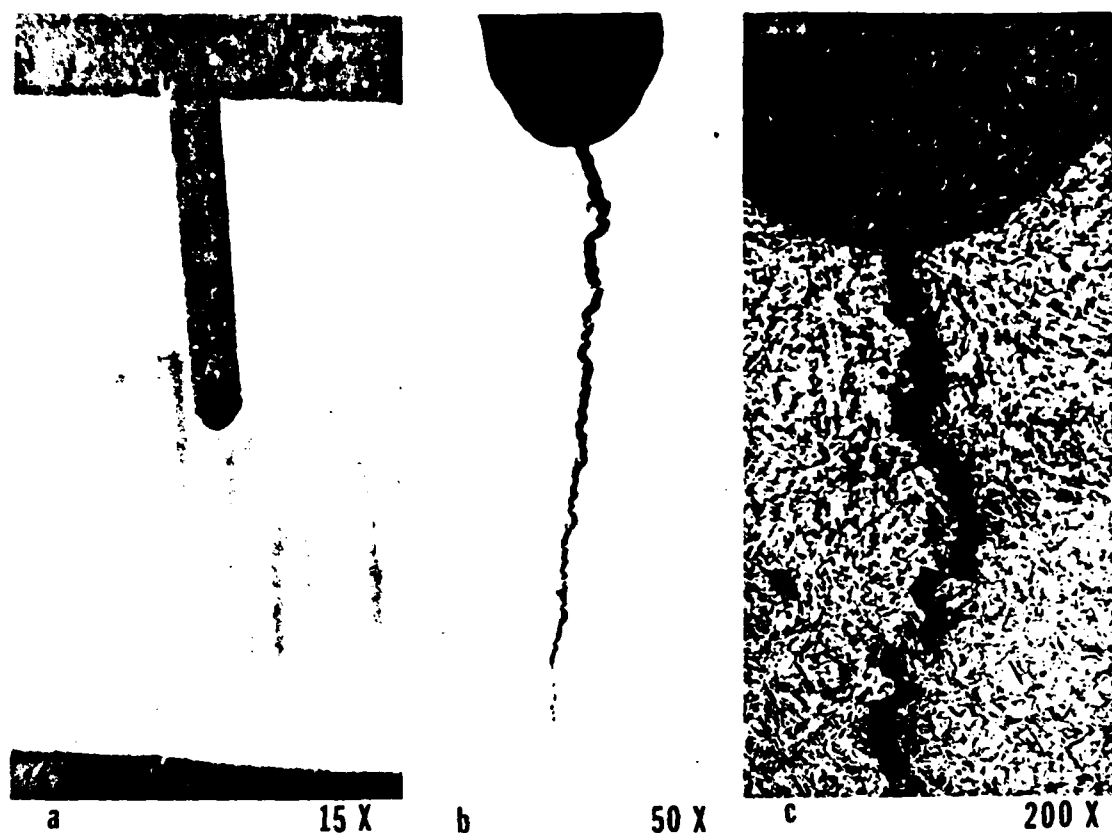


Figure 4. Photomicrographs of notched and Cu-plated specimens of gun steel after capacitive-discharge pulse heating to around 1000°C.

Gleeble Hot-Tensile Testing

Direct evidence for the embrittlement of gun steel by copper was also obtained using a Gleeble Model 1500 hot-tensile testing machine. Specimens, one-half inch in diameter, were machined from gun steel and Cu-plated over the reduced cross-section using masking tape. Specimens were pulled at nominal center temperatures of 1000, 1050, and 1100°C at various strain rates around 10^{-1} to -10^{-1} per minute. In a few cases, attempts to stop the tests prior to complete rupture were successful.

Macrophotographs of a Cu-plated sample pulled at 1100°C at a strain rate of $10^1/\text{min.}$ are shown in Figure 5. The occurrence of classical hot-tearing due to an embrittling agent is quite evident. No indication of hot-tearing was found on specimens that were not Cu-plated but were tested under similar conditions. The depth of penetration of the hot-tears varied considerably. Scanning electron micrographs of a longitudinal section of the 1100°C Gleeble specimen are shown in Figure 6. X-ray spectrochemical analysis in the SEM confirmed the presence of Cu at the tip of the cracks as is demonstrated by the inset on the figure.

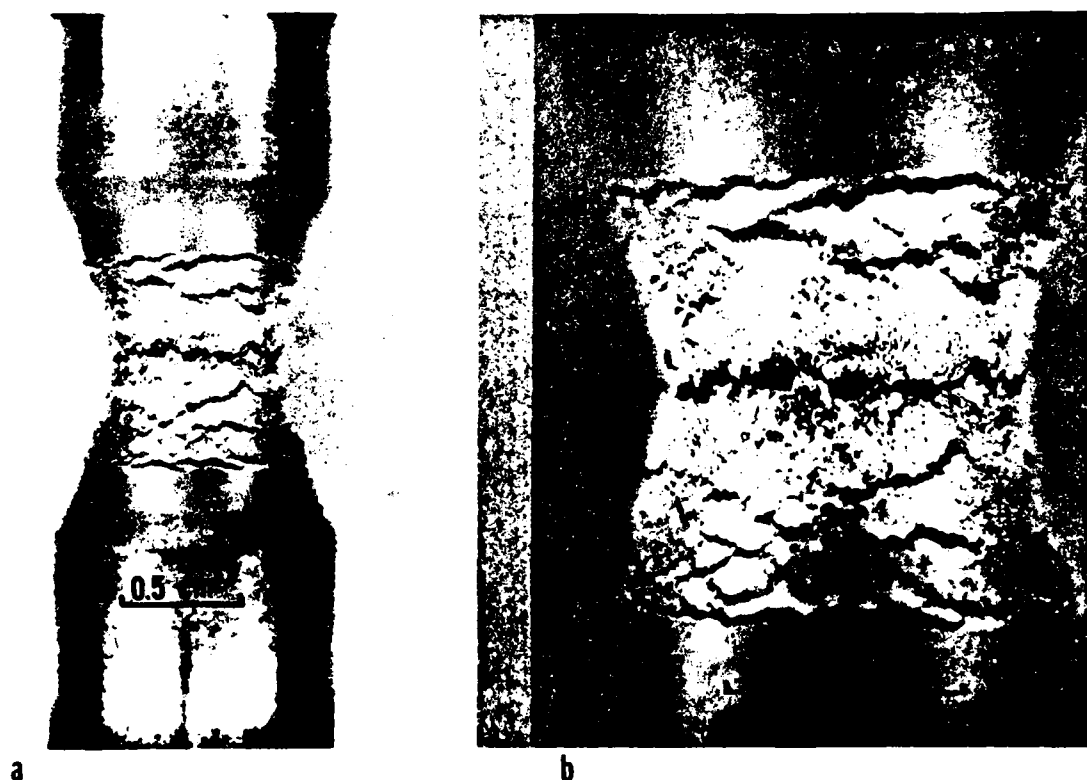


Figure 5. Photomicrographs of a sample of Cu-plated gun steel pulled at 1100°C in a Gleeble hot tensile machine.

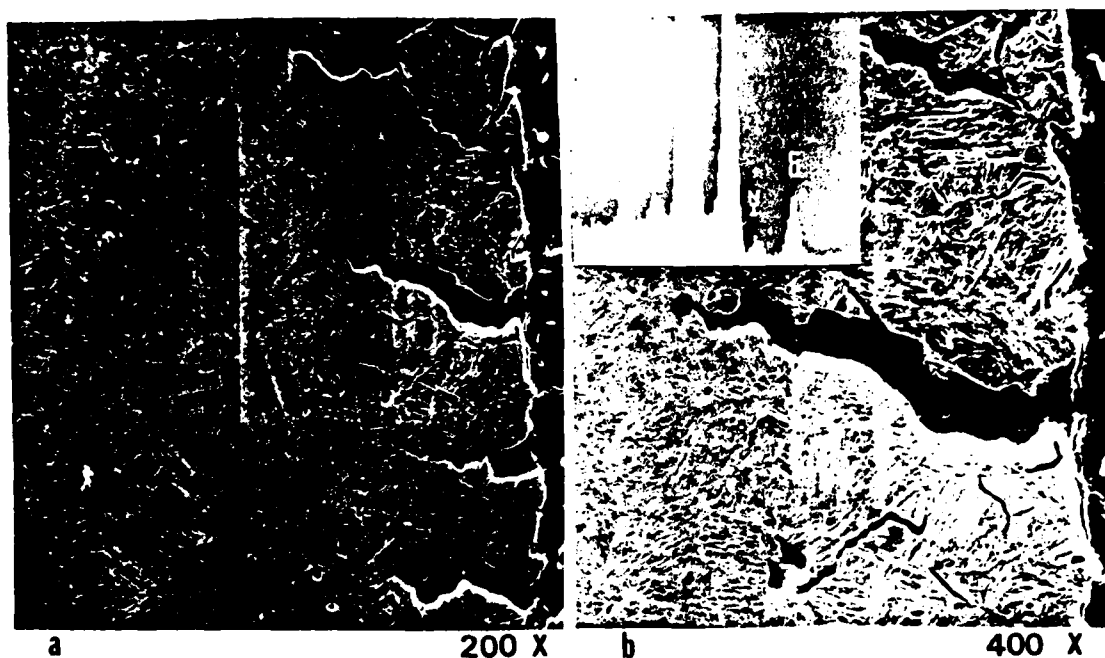


Figure 6. Scanning electron micrographs of cross-section of 1100°C Gleeble specimen shown in Figure 5. X-ray specimen illustrates the occurrence of Cu at the tip of the rupture.

Metallographical examination of areas between the deep fissures shown in the macrograph provided information about the distribution of Cu ahead of the ruptures. A good example is illustrated by the SEM and Cu x-ray maps in Figure 7 which shows a high concentration of Cu in a prior austenite grain boundary. Another example of grain boundary Cu is shown at higher magnification in Figure 8. Computer-processing of the x-ray signal to improve contrast and definition serves to enhance the image of the Cu concentration as shown in the x-ray map of Figure 8(b).

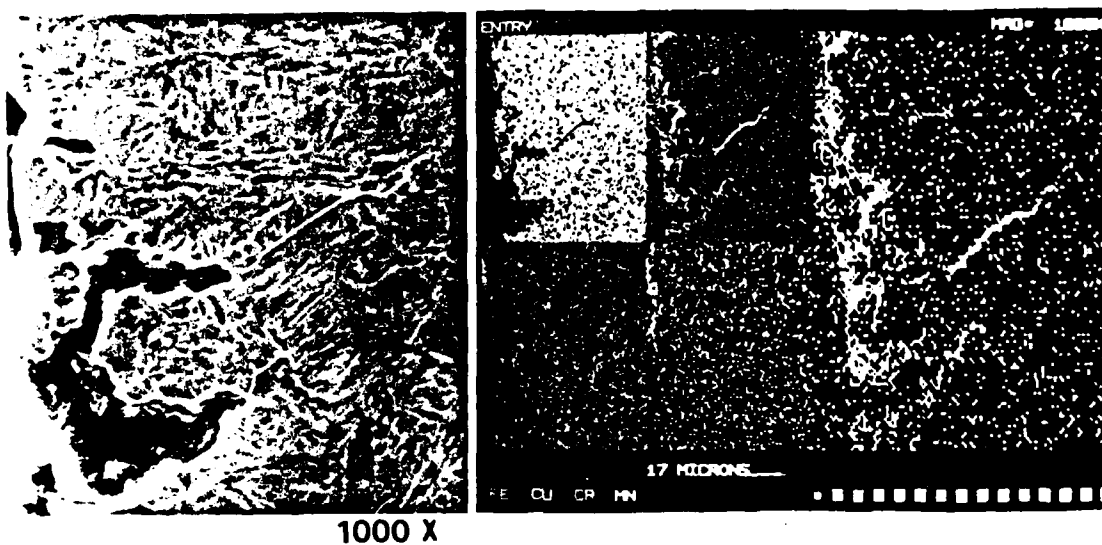


Figure 7. Scanning electron micrograph of 1100°C Gleeble specimen and x-ray maps showing high concentration of Cu well ahead of the cracks.

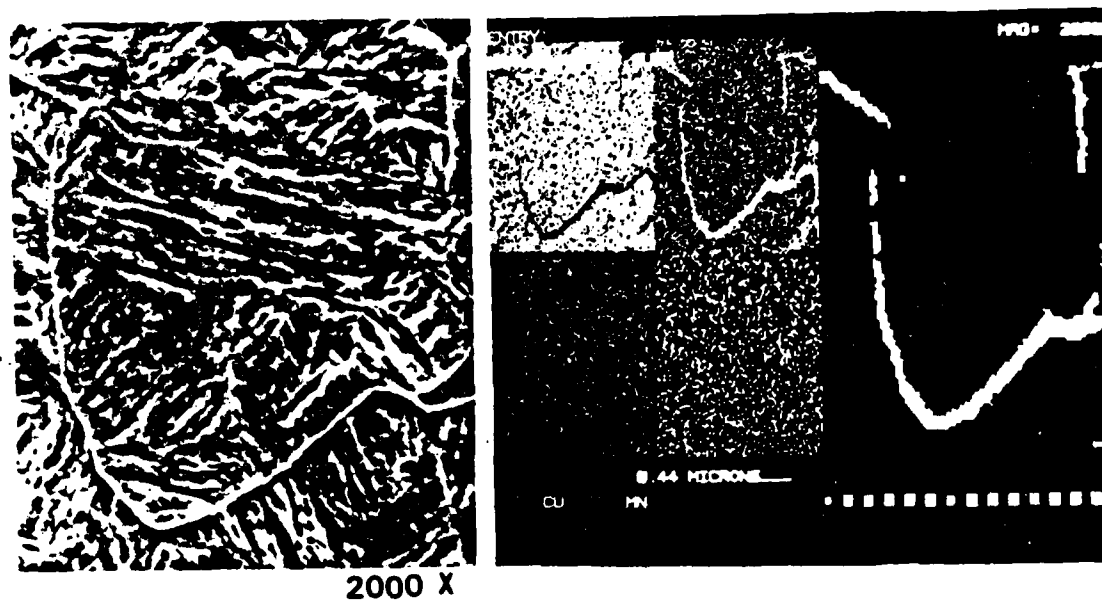


Figure 8. (a) Scanning electron micrograph of 1100°C Gleeble specimen, and (b) computer-processed x-ray map showing presence of Cu in prior austenite grain boundaries.

The effect of temperature on Cu embrittlement during Gleeble hot-tensile testing was investigated by running a few specimens at 1000°C and 1050°C. Examples of samples of gun steel strained at 1050°C with and without Cu-plating are shown in Figure 9. (The temperature, which refers to the reading of the thermocouple attached to the center of the gauge length, is lower at the limits of the reduced cross-section.) It is very clear that the effect of Cu on hot-tearing is very pronounced even below its melting point. Generally, similar results were obtained at 1000°C. The scanning electron micrograph (Figure 9(c)) illustrates the highly strained structure that develops near the the apex of the fracture core. In the case of the Cu-plated sample, decohesion of the grain boundaries occurs so that the individual grains, or small clusters, remain in place - largely undeformed, while the interior region - unaffected by copper, deforms plastically. In the absence of Cu, the surface and interior grains deform homogeneously. This effect is very similar to the separation of polycrystalline aluminum into individual grains using gallium that is described by Rhines and Gokhale (ref 5).

SUMMARY OF EXPERIMENTAL OBSERVATIONS

The relevant experimental findings are as follows: (1) Copper is transferred by abrasion from the Cu rotating band on the projectile to the surface of the cannon tube. (2) The copper penetrates heat-check cracks that

⁵F. N. Rhines and A. B. Gokhale, "Measurement of Topology and Size Distribution of Grains in Aluminum by Penetration With Liquid Gallium," Liquid and Solid Metal Embrittlement, M. H. Kamdar, Ed., AIME, June 1984.

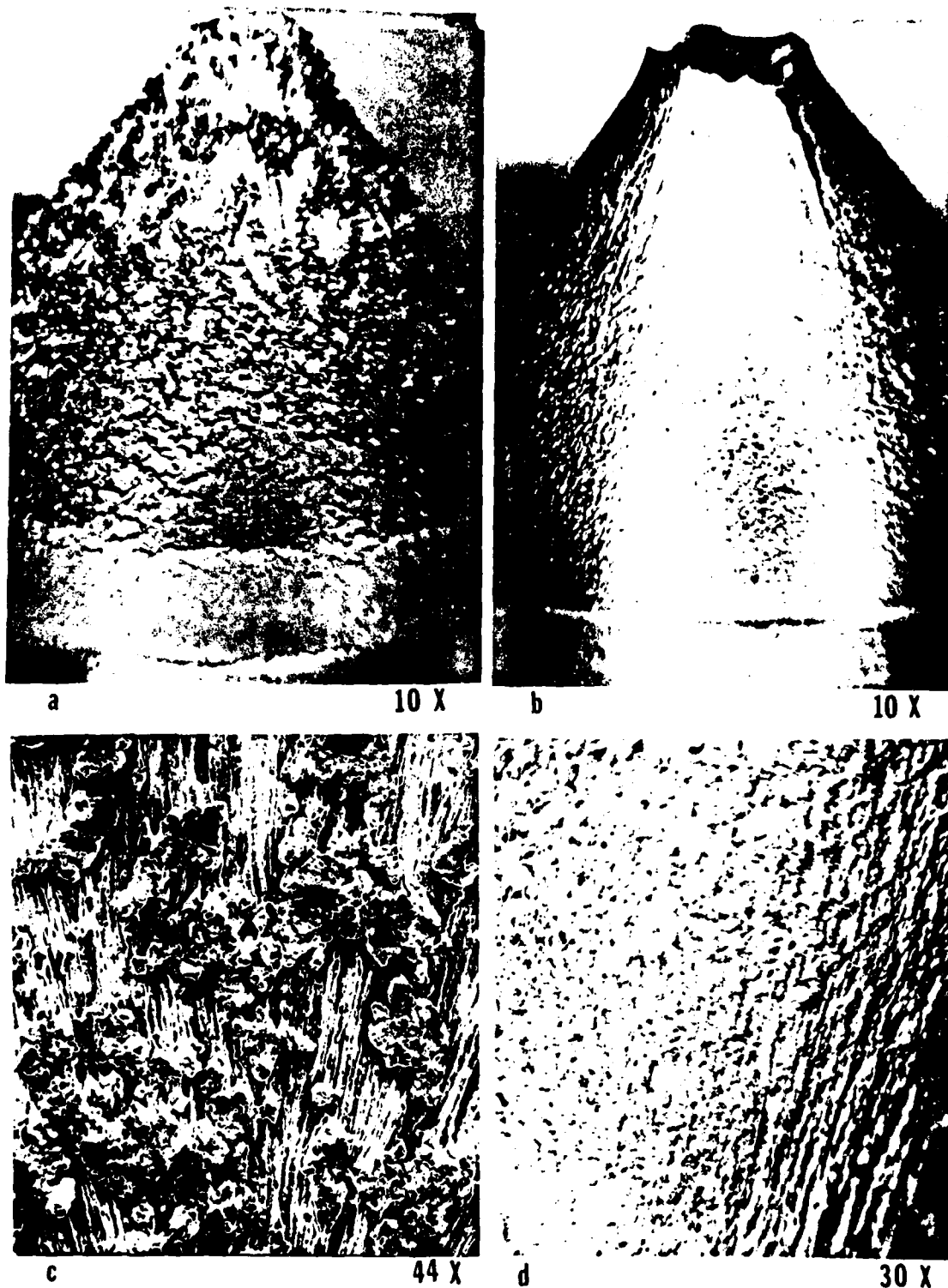


Figure 9. Photomicrographs (a,b,d) of 1050°C Gleeble specimens and scanning electron micrograph (c); a,c = Cu-plated, b,c = not plated.

are caused by rapid heating and cooling during and after firing. (3) The growth of some of the heat-check cracks into deep penetrating fatigue cracks is enhanced by Cu-embrittlement. (4) Cu-embrittlement can occur during heat pulses of only a few milliseconds duration. (5) Cu-embrittlement can occur at temperatures of 1000°C or less, i.e., well below the melting point of Cu. (6) Cu penetrates prior austenite grain boundaries well ahead of surface cracks.

DISCUSSION

The metallographic studies of both fired cannon samples and specimens pulse heated or rapidly strained in the laboratory show direct correlation between the presence of copper and cracking of the surface. Both of these situations are very different from the usual occurrence of hot-shortness due to copper (ref 6). In hot-shortness, the copper segregation is the result of preferential scaling of the steel resulting in a buildup of copper at the interface until it exceeds the solubility of austenite and forms metallic copper. Above its melting point, the copper can weaken the grain boundaries and cause rupture of the surface in the presence of tensile stresses during rolling or other mechanical working processes. Another major difference with hot-shortness due to copper that may occur during hot-rolling of steel is that the surface will be above the melting point of copper for just a few milliseconds. Despite the very brief duration of the exposure to liquid

⁶D. A. Melford, "The Influence of Residual and Trace Elements on Hot-Shortness and High Temperature Embrittlement," Phil. Trans. R. Soc., London, A295, 1980, pp. 89-103.

copper and the very steep temperature gradient below the surface, copper is present right to the tips of the cracks.

In summary, the embrittling effects of copper, commonly associated with hot-working processes are also evident when metallic copper is in contact with steel at high temperatures and in the presence of tensile stresses. In some cases, the embrittlement is due to classical reduction in cohesion at the grain boundary by the presence of liquid copper. However, penetration of copper along grain boundaries (ref 7) below its melting point can also result in reduction in the grain boundary cohesion (refs 8-10) and rupture. Constant temperature and fixed load testing are required to establish the minimum temperature for solid metal embrittlement by copper. Cracks initiated by Cu liquid-solid metal embrittlement may continue to propagate during cooling under the influence of thermally-induced stresses.

⁷G. R. Speich, J. A. Gula, and R. M. Fisher, "Diffusivity and Solubility Limit of Copper in Alpha and Gamma Iron," in The Electron Microprobe, T. D. McKinley, K. F. J. Heinrich, and D. B. Witty, Eds., Symposium of the Electrochemical Society, Washington, D.C., October 1974, pp. 525-542.

⁸N. S. Stoloff, "Metal Induced Embrittlement - A Historical Perspective," Liquid and Solid Metal Embrittlement, M. H. Kamdar, Ed., AIME, June 1984.

⁹M. H. Kamdar, "Liquid Metal Embrittlement," Embrittlement of Engineering Alloys, C. L. Briant and S. F. Banarji, Eds., Academic Press, New York, 1983.

¹⁰C. L. Briant and R. P. Messmer, "Chemical Bonding and Grain Boundary Embrittlement," Liquid and Solid Metal Embrittlement, M. H. Kamdar, Ed., AIME, June 1984.

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